NANOSTRUCTURE MATERIALS FOR RECHARGEABLE LITHIUM-ION AND LITHIUM-OXYGEN BATTERIES

A thesis presented for the award of the degree of

Doctor of Philosophy

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By Bing Sun, B. Eng., M. Eng.

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DEDICATION

This thesis is dedicated to my parents.

CERTIFICATION

I, Bing Sun, declare that the work in this thesis has not previously been submitted for a degree nor has it been submitted as part of requirements for a degree except as fully acknowledged within the text.

I also declare that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis has been acknowledged. In addition, I declare that all information sources and literature used are indicated in the thesis.

Bing Sun

02-07-2012

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LIST OF ABBREVIATIONS

Abbreviation	Full name
a.u.	Arbitrary unit
BET	Brunauer Emmett Teller
CB	Carbon black
cm	Centimeter
CMC	Dimethyl carbonate
C-rate	Current rate
EC	Ethylene carbonate
EIS	Electrochemical impedance spectroscopy
Eq.	Equation
FESEM	Field emission scanning electron microscopy
FTIR	Fourier transform inferior red spectroscopy
EVs	Electric vehicles
HEVs	Hybrid electric vehicles
HF	Hydrofluoric acid
JCPDS	Joint committee on powder diffraction standards
Li	Lithium
nm	Nanometer
NMP	1-methyl-2-pyrrolidinone
OCP	Open circuit potential
PC	Propylene carbonate
PTFE	Polytetrafluoroethylene
PVDF	Polyvinylidene fluoride
SAED	Selected area electron diffraction
SEI	Solid electrolyte interphase
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
XRD	X-ray diffraction

LIST OF PUBLICATION

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ABSTRACT

Electrode materials and catalysts are key factors influencing the high power and high efficiency performances of lithium-ion batteries or lithium-oxygen batteries. In this doctoral work, a series of nanostructure materials, such as one-dimensional nanorods, two-dimensional nanoplates and nanosheets, three-dimensional microspheres and mesoporous structures, were successfully synthesized by various methods. Their electrochemical performance in lithium-ion batteries and lithium-oxygen batteries was also measured by galvanostatic charge-discharge, cyclic voltammetry and electrochemical impedance spectra.

$LiFePO_4$ facet nanoplates/graphene hybrid materials and mesoporous nanolayer carbon coated $LiFEPO_4$ microspheres were synthesized by a hydrothermal method combined with high temperature treatment. The as-prepared materials exhibited both high discharge capacities and excellent high-rate performances as cathode materials for lithium-ion batteries.

Mesoporous α-Fe_2O_3 was successfully synthesized by a soft template method for testing as an anode material in lithium-ion batteries. The as-prepared mesoporous α-Fe_2O_3 electrodes showed a high discharge specific capacity and stable cycleability. The excellent electrochemical performance should be attributed to the unique mesostructure, with its high surface area able to provide high surface contact with the electrolyte and decrease the current density per unit area.

One-dimensional MnO/C core-shell nanorods were successfully prepared from the reduction of MnO_2 nanowires. This material exhibited good electrochemical performance as an anode material for lithium-ion batteries, which is higher than that of MnO microparticle and MnO_2 nanowire electrodes. A one-dimensional nanorod structure can greatly shorten the pathways for lithium ion diffusion. The nanoporous carbon coating layer greatly increased the electronic conductivity of the composite.

Graphene nanosheets (GNSs) were prepared by a chemical reduction reaction and directly used as cathode catalysts for lithium-oxygen batteries with an alkyl carbonate electrolyte. The as-prepared GNSs electrode exhibited better cyclability and lower over-potential than that of the Vulcan XC-72 electrode. The reduced over-potential shows the as-prepared GNSs, with many carbon vacancies and defects on their surfaces, were more electrochemically active than Vulcan XC-72 in an alky carbonate electrolyte.

Mesoporous CoO/CMK-3 nanocomposite was synthesised by an impregnation method using the mesoporous carbon CMK-3 as the template. When used as the cathode catalyst in lithium-oxygen batteries, the as-prepared CoO/CMK-3 nanocomposite electrode exhibied better capacity retention than that of bare mesoporous CMK-3 carbon, Super-P or CoO/Super-P nanocomposite. The mesopores inside the CoO/CMK-3 nanocomposite facilitate the diffusion of oxygen during the discharge process and the release of the charge products during the charging process. The CoO nanoparticles significantly reduce the charge over-potential and increase the round-trip efficiency.

INTRODUCTION

Global warming, limited supplies of fossil-fuel, and increasing city pollution make the urgency for replacing petroleum with clean energy sources (wind, solar, tidal) greater ever before. CO_2 emission, and consequent air pollution, can be reduced by replacement of internal combustion engine (ICE) cars with zero emission electric vehicles (EVs). Energy storage has become more important today than at any time in human history.

Current lithium-ion batteries have proved themselves the most advanced electrochemical power sources for portable electronic devices in the past two decades. However, they cannot meet the stringent requirements for high power in electric vehicles (EVs) and hybrid electric vehicles (HEVs). Intensive research is continuing on all aspects of lithium-ion batteries including, cathode materials, anode materials, binder, electrolytes and the battery production technique. The active materials of the electrode are key to increasing lithium-ion battery energy density and power density above the energy and power densities of current lithium-ion batteries. Commercial lithium-ion battery electrodes are composed of powders containing micro-sized particles which seriously limit lithium ion diffusion. Fortunately, nanotechnology has paved the way for advanced electrode materials to achieve high-power performance. In this doctoral work, nanostructure materials for both cathode and anode electrodes have been developed.

However, even when fully developed, the highest energy storage of current lithium-ion batteries still cannot meet the demands of key markets, such as transport, in the long term. Recently, rechargeable lithium-oxygen batteries have been attracting more and more attention and are considered an option as the power source for electric vehicles. This new configuration of lithium batteries can store 3-4 times higher energy than the state-of-the-art lithium-ion batteries. The development of an efficient air electrode is a huge challenge for lithium-oxygen batteries. The use of nanostructure carbon materials and nanocomposites has shown great potential for improving the electrochemical performance of lithium-oxygen batteries.

The purpose of this doctoral work is to discuss possible ways of improving the electrochemical performance of rechargeable lithium batteries via the use of nanostructure materials and to provide possible opportunities for future research directions. A series of nanostructure materials, such as one-dimensional nanorods, two-dimensional nanoplates and nanosheets, three-dimensional microsphere and mesoporous structures, were successfully synthesized by hydrothermal methods, soft template methods, hard template methods and chemical reduction methods. The morphologies of the as-prepared materials were characterized by scanning electron microscopy and transmission electron microscopy. The electrochemical performance of the as-prepared materials was evaluated by various electrochemical measurements; they were tested for their use as electrode materials for lithium-ion batteries or for their use as as catalysts for lithium-oxygen batteries. The dynamic behavior of lithium ion diffusion in the electrode was investigated to reveal the mechanisms behind any observed improvement in electrochemical performance. Increased electrocatalivity of the electrochemical reaction in the cathode of lithium-oxygen batteries will be discussed.

An outline of the content is briefly presented as follows:

1. A literature review of lithium-ion batteries and lithium-oxygen batteries is presented in Chapter 1. In this chapter, the basic concepts and principles of lithium-ion batteries are presented. Recent developments in the conventional cathode materials and anode materials for lithium-ion batteries are reviewed. The architectures, electrochemical reactions and the development of cathode catalysts of lithium-oxygen batteries are also introduced.
2. Chapter 2 contains the experimental parts, including the material synthesis methods, physical and structural characterization methods, electrode preparation and electrochemical characterization methods. The synthesis methods include hydrothermal methods, soft template methods, hard template methods and chemical reduction methods. X-ray diffraction and Raman spectroscopy were used to identify the crystal structure of the as-prepared materials. The morphology and particle size distribution were observed by field emission gun scanning electron microscopy and transmission electron microscopy. The carbon content was determined by thermogravimetric analysis. The electrochemical performance was evaluated by

galvanostatic charge-discharge, cyclic voltammetry (CV) and electrochemical impedance spectra.

3. To achieve high-power performance for lithium-ion batteries, $LiFePO_4$ nanostructures were synthesized and used as cathode materials in lithium-ion batteries. As detailed in chapter 3, novel $LiFePO_4$ facet nanoplates/graphene hybrid materials were synthesized by a hydrothermal reaction combined with high temperature treatment. As detailed in Chapter 4, mesoporous nanolayer carbon coated $LiFePO_4$ microspheres were prepared by a hydrothermal method.

4. One-dimensional core-shell MnO nanorods and three-dimensional mesoporous α-Fe_2O_3 were also synthesized and evaluated as high capacity anode materials for lithium-ion batteries. As detailed in Chapter 4, core-shell MnO nanorods were synthesized by reducing MnO_2 nanowires in a reductive atmosphere combined with an in-situ carbon coating technique. As detailed in Chapter 5, mesoporous α-Fe_2O_3 was synthesized by a soft template method using tri-block copolymer F-127 as the template.

5. The effect on the electrochemical performance of lithium-oxygen batteries of using nanostructure materials as cathode catalysts is discussed. As detailed in Chapter 7, graphene nanosheets were used as cathode catalysts and were found to be more active than other forms of carbon towards the electrochemical reaction in lithium-oxygen batteries. As detailed in Chapter 8, a nanocasting technique was used to synthesize mesoporous carbon CMK-3. CoO nanoparticles were loaded on

the CNK-3carbon through an impregnation method. The CoO/CMK-3 nanocomposite was measured as a cathode catalyst for lithium-oxygen batteries.